Orbital-quenching-induced magnetism in Ba$_2$NaOsO$_6$

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Abstract. - The double perovskite Ba$_2$NaOsO$_6$ with heptavalent Os (d^1) is observed to remain in the ideal cubic structure (*i.e.* without orbital ordering) despite single occupation of the t_{2g} orbitals, even in the ferromagnetically ordered phase below 6.8 K. Analysis based on the *ab initio* dispersion expressed in terms of an Os t_{2g}-based Wannier function picture, spin-orbit coupling, Hund's coupling, and strong Coulomb repulsion shows that the magnetic OsO$_6$ cluster is near a moment-less condition due to spin and orbital compensation. Quenching (hybridization) then drives the emergence of the small moment. This compensation, unprecedented in transition metals, arises in a unified picture that accounts for the observed Mott insulating behavior.

Orbital physics in transition metal oxides has attracted a good deal of attention for three decades, with much of the activity focused on coupling to spin, charge, and lattice degrees of freedom in d^1 systems. The d^1 configuration is typically found in the early 3d transition metals (TMs), *i.e.* titanates and vanadates, and the associated phenomena – often revolving around the tendency to orbitally order – are remarkably rich. The d^1 configuration can also occur in the mid- to late-5d TM ions, which are distinguished also by unusually high formal valence states.

Unless fully itinerant, partially filled d shells lead to non-spherical ions that often are accommodated by orbital ordering (OO), that is, ordered alignment of the filled orbitals [1,2] in the manner that minimizes strain, electronic, and magnetic energies. [3] An outcome is that OO has been identified as the driving mechanism in symmetry-breaking structural and magnetic transitions, [2] and may also be coupled to magnetism and charge order, the Mott insulating d^1 perovskite YTiO$_3$ being a well studied example. [4] Very different behavior is shown by the d^1 system LaTiO$_3$ which has a structural distortion although evidence of OO has been difficult to obtain. A prominent explanation is that orbital fluctuations dominate, leading to a disordered *orbital liquid* ground state. [5,6]

Double perovskite structure Ba$_2$NaOsO$_6$ (BNOO) is a rare example of a heptavalent osmium compound, also rare because it is a ferromagnetic insulator [7–9] (T$_C$ = 6.8 K), and it shows other perplexing behavior. Although it has a single 5d electron in the t_{2g} complex that orders magnetically, it shows no evidence of orbital order that would destroy its cubic symmetry. On the other hand, the sister compound La$_2$NaOsO$_6$ with high-spin d^3 Os configuration with nominally cubic symmetry is observed to be highly distorted, [10] which is ascribed to misfit arising from the small cation radius. The question of spin ordering surely is a delicate one, since isostructural and isovalent Ba$_2$LiOsO$_6$ (BLOO) orders *anti*ferromagnetically in spite of a very similar Curie-Weiss susceptibility [7] and nearly identical volume.

The question of formal valence, and identification of several material constants, can be identified from first principles local density approximation (LDA) calculations using two all-electron full-potential electronic methods of FPLO and Wien2k. [11–14] The Fermi level E$_F$ lies within the t_{2g} bands, confirming the heptavalent nature of the Os ion. A crystal (ligand) field splitting of almost 5 eV separates the centroids of the e_g and t_{2g} bands, reflecting the unusually strong 5d − 2p hybridization, and a gap of roughly 1.5 eV separates the t_{2g} symmetry bands from the more tightly bound O 2p-dominated OsO$_6$ cluster orbitals, with gaps separating various degenerate molecular orbitals. [15,16]

Several complications must be taken into account to obtain a realistic picture of the electronic structure. (i) The strong hybridization of Os 5d orbitals with O 2p states, which has ramifications in this double perovskite structure beyond the usual ones in oxides. (ii) Strong spin-orbit coupling (SOC) on the Os site has important consequences. (iii) Hund's (exchange) coupling effectively se-
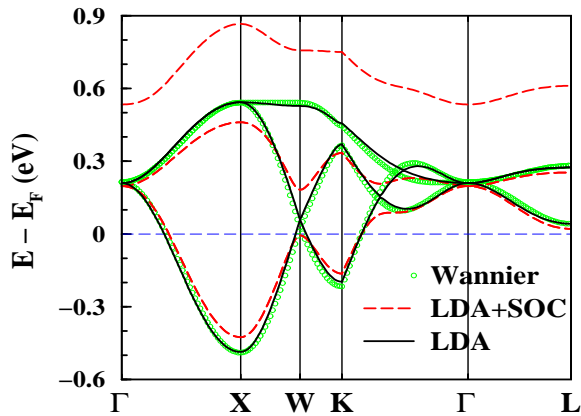
Fig. 1: (color online) Nonmagnetic Os t_{2g} band structure in LDA, in three Wannier orbital representation (tight binding [TB]), and LDA+SOC, relative to the Fermi level E_F. In LDA, the top of the t_{2g} manifold is very flat near the Γ point and along the X-W line, resulting in very sharp peaks just above E_F in the density of states (see fig. 2). From LDA+SOC, the spin-orbit coupling constant ξ is 0.30 eV.
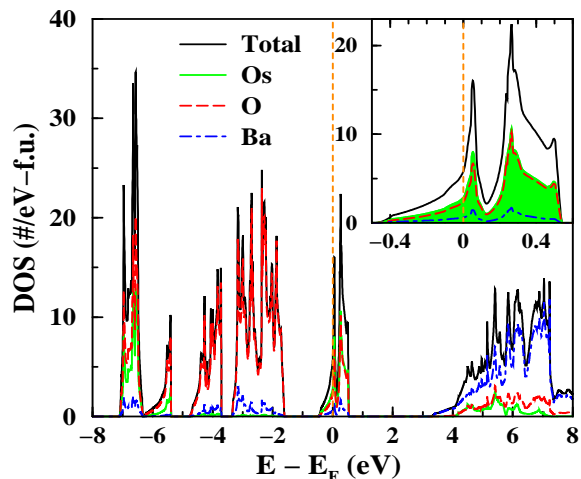

Fig. 2: (color online) Total and atom-projected densities of states (DOS) per formula unit for nonmagnetic state in LDA. The vertical dashed line indicates the Fermi energy. Inset: Blowup near E_F. It displays that contribution of six oxygens is nearly similar with Os character in the t_{2g} manifold. As a result, it is anticipated that the oxygens significantly contribute to magnetic moment.

lects the occupied orbital. (iv) Intra-cluster Coulomb repulsion, which is the obvious suspect for a magnetic insulating state in an open shell system. Finally, it is likely that quantum fluctuations may also play an important role in determining the observed behavior. While the interplay of spin and orbital physics has been addressed in considerable detail, [17] the large SOC in BNOO puts this compound in a distinct class relative to the early 3d systems.

The unusual aspects of BNOO then are: a Mott insulating state based on a localized d^1 ion that nonetheless retains a cubic environment, and a small ordered moment in a 3D system where fluctuation effects typically are minor. It is most instructive to consider the various aspects of the electronic structure consecutively. We build an understanding of the electronic structure and competing mechanisms in a different manner from Xiang and Whangbo [18] in their study of BNOO.

Isolated t_{2g} bands: cluster orbitals. The t_{2g} bands, with bandwidth W=1.05 eV, form a self-contained system for the purpose of understanding the low energy, low temperature physics. The three bands can be represented accurately in a Wannier function basis with three first neighbor d-d hopping parameters (in meV) $t_\sigma = -121, t_\pi = 64, t_\delta = 24$ meV, with on-site energy $\varepsilon = 202$. (For BLOO $t_\sigma = -131$ is the only change.) Note that t_δ is necessary to give the excellent representation of the bands shown in fig. 1. The corresponding total and atom-decomposed densities of states (DOS) are pictured in fig. 2, which reveals the isolation of the narrow t_{2g} bands. As pointed out by Erickson *et al.* [8] the overlap takes place between O $2p_\pi$ orbitals on neighboring OsO$_6$ octahedra; these O orbitals comprise the 'tails' of the t_{2g} symmetry cluster orbitals. The Fermi level lies 0.5 eV (one electron) up

into the bands. The DOS shown in fig. 2 is highly nonsymmetric about their center, with 2/3 of the weight lying in the upper half of the bands.

As analyzed in some detail by Singh and coworkers [15, 16] in the context of pentavalent Ru in Sr$_2$YRuO$_6$ which also contains a closed shell ion (Y^{3+}) in one of the cation sites, the OsO$_6$ unit should be approached as an isolated cluster. The Os t_{2g} states generalize to cluster orbitals with the Os $5d_{xy}$ state (say) bonded to the p_π orbitals lying in the $x - y$ plane. We calculate that half of the density of the t_{2g} bands lies on Os, the other half distributed amongst four p_π orbitals, and the cluster orbital (with symmetric partners $\mathcal{D}_{xz}, \mathcal{D}_{yz}$) is

$$\mathcal{D}_{xy} \approx \sqrt{\frac{1}{2}} d_{xy} + \sqrt{\frac{1}{8}} \sum_{j=1}^{4} p_{\pi,j}. \tag{1}$$

This cluster orbital aspect, adopted also by Erickson and collaborators, [8] is central to the following analysis. The overlap of these cluster orbitals is what is described by $t_\sigma, t_\pi, t_\delta$.

Tendency toward magnetism. Xiang and Whangbo reported [18] obtaining a FM ground state for BNOO. Checking out this question with progressively finer k-point samplings of the zone, we find BNOO is not quite unstable to a FM state. For meshes of 8×8×8 or finer, the magnetic moment that is obtained on coarser meshes vanishes. Thus the Stoner interaction constant can be obtained from the condition of (near) fulfillment of the Stoner instability: $I_{st} = 1/N(E_F) = 0.35$ eV [The Fermi level density of states $N(E_F)$=2.88 states/eV per spin]. As will also be the case for the SOC strength (below), it is important
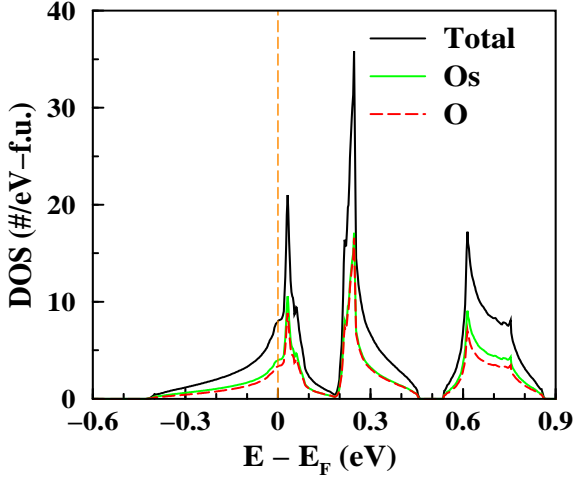
Fig. 3: (color online) Total and atom-projected DOS per formula unit, with spin-orbit coupling included. Oxygen contribution is 50% throughout the bands. The two lower bands are distinct, and nearly disjoint, leading roughly to a half-filled single-band configuration.

that this parameter is not evaluated from the Os atomic potential alone, because the relevant local (molecular) orbital is only half Os $5d$, and I_{st} is reduced accordingly. The Hund's (exchange) splitting for a fully polarized d^1 orbital is $\mathcal{J}_H \approx I_{st} = 0.35$ eV, which is smaller than the bandwidth but comparable to the SOC strength (see below).

Spin-orbit coupling. It has been known for fifty years [19–21] that the t_{2g} complex can be mapped onto an angular momentum $\vec{L} \to -\vec{\mathcal{L}}$ with quantum number $\mathcal{L}=1$, so within these bands the SOC operator becomes $-\xi\vec{\mathcal{L}}\cdot\vec{S}$ with $\xi > 0$. The basis $\{\mathcal{D}_{xy}, \mathcal{D}_{yz}, \mathcal{D}_{zx}\}$ can be mapped onto the $\mathcal{L}_z$ eigenstates to $|0\rangle \to \mathcal{D}_{xy}$; $|\pm 1\rangle \to \mathcal{D}_{zx} \pm i\mathcal{D}_{yz}$, where the integer denotes the angular momentum projection $m_{\mathcal{L}}$ onto $\hat{z}$. The negative sign leads to an inverted spectrum, with the $J = \frac{3}{2}$ quartet at $-\xi/2$ and the $J = \frac{1}{2}$ doublet at $+\xi$. The calculated splitting at $k=0$ gives a large SOC strength $\xi=0.30$ eV, so large it splits off the entire upper $J=1/2$ band as is clear from fig. 1.

The DOS with SOC included is displayed in fig. 3. In addition to the split-off upper $J = \frac{1}{2}$ band, the lower two bands are nearly disjoint, being bound together only by the degeneracy within the $J = \frac{3}{2}$ states at zero momentum(fig. 1). As a result, the problem of the Mott insulating state does not rigorously reduce to a single band problem though it may be effectively single band. As a result of the mapping $\vec{L} \to -\vec{\mathcal{L}}$ within the t_{2g} states of interest, the total angular momentum is $\vec{J} = \vec{S} - \vec{\mathcal{L}}$ ($J = \frac{1}{2}, \frac{3}{2}$), the magnetic moment is $\vec{M} = \mu_B(2\vec{S} - \vec{\mathcal{L}})$, and the g-factor is $g_J = \frac{3}{2} - \frac{5}{8J(J+1)}$. In this isolated cluster limit, the r.m.s. moment $(\vec{M}^2)^{1/2}$ is small (1 μ_B) for $J = \frac{1}{2}$ but is larger ($\sqrt{7}\mu_B$) in the $J = \frac{3}{2}$ ground state.

At the band structure level, there remains only the

Hund's exchange splitting $H_{ex} = -\mathcal{J}_H S_z$ due to the Os moment, which becomes important because this interaction lifts the remaining degeneracies. The lowest state at $k=0$ is

$$|m_{\mathcal{L}} m_S\rangle = |+1\uparrow\rangle \propto |[\mathcal{D}_{zx} + i\mathcal{D}_{yz}]\uparrow\rangle. \qquad (2)$$

but the dispersion leads to overlapping bands and metallicity, so intra-cluster Coulomb repulsion effects are required to describe the observed insulating character, as also concluded by Xiang and Whangbo.

Intra-atomic versus intra-molecular repulsion: the Mott insulating state. For a lattice of d^1 ions in t_{2g} orbitals, an on-site Hubbard repulsion of roughly $U \sim W$ is expected to lead to a Mott insulating state. To model this insulating state we initially applied the correlated band LDA+U method, using $J=1$ eV (whose value seemed immaterial) and varying U. Since the initial interest was to look for an orbitally ordered solution, the full rotationally-invariant form of interaction implemented in Wien2k was used, and (following conventional practice) the U (and J) interaction is applied only to the Os $5d$ orbitals. A Mott insulating state was *not obtained* for values of U even several times larger than W. At $U=4$ eV $\approx 4W$ the increasing exchange splitting leads only to a half metallic state, not an insulating state.

This failure of the LDA+U method, as conventionally applied to atomic orbitals, to produce the expected Mott insulating state is a situation we have observed previously in $4d$ and $5d$ oxides. The problem can be cast not as a failure of the LDA+U approach *per se*, but rather of its application to an extended *cluster* orbital by applying the orbital potentials solely to the Os $5d$ *atomic* function, rather than the entire molecular orbital $\mathcal{D}$. Since only 50% of the $\mathcal{D}$ orbital's charge is Os $5d$, the LDA+U correction tends mainly to change the relative amounts of $5d$ and $2p$ character, rather than to open a gap by shifting the energy of a cluster orbital. As a result, no state with integer $5d$ occupation number can arise, whereas in the LDA+U method integer occupation is necessary to obtain the insulating state. This problem is cured by using the Wannier basis, rather than the atomic state basis, in the LDA+U method.

The full correlated electronic structure. The unfolding of the electronic structure that we find most instructive is pictured in fig. 4. We begin from the basis of degenerate orthonormal cluster orbitals (H_0), include SOC interaction H_{SOC}, then account for Hund's (exchange) interaction $\mathcal{J}$ that breaks the degeneracy, and finally the repulsive Coulomb interaction H_U (as in LDA+U)

$$H = H_0 + \xi\vec{L}\cdot\vec{S} - \mathcal{J}_H\hat{S}_z + H_U. \qquad (3)$$

All of these are single site, and therefore simple to visualize. Kinetic effects (banding) is a small effect that enables charge transfer, but when it does not destroy the gap, as here, it is the least significant.

Table 1: Values of spin, orbital, and total moments versus the value of U, within the correlated t_{2g} shell of BNOO. Increasing the hopping t parameters (by 50-100%) reduces the individual moments but hardly changes the net moment.

U	M_S	M_L	M_{tot}
1.1	0.714	-0.717	-0.003
1.5	0.909	-0.866	+0.043
2.0	0.976	-0.935	+0.041

Fig. 4: Evolution (schematic) of the t_{2g} energies from isolated 3×2-fold degenerate for the isolated ion (in its cubic environment), through SOC, Hund's coupling, Coulomb repulsion U, and finally dispersion due to hopping t. The occupied band has pure spin-orbital $|+1\uparrow\rangle$ character until intercluster hopping is included.

As mentioned above, Hund's exchange lowers the pure spin up $|+1\uparrow\rangle$ member of the lower spin-orbit quartet, making it the orbital to occupy to achieve the lowest energy. Then Coulomb repulsion lowers this occupied state by $\sim U$ with respect to the others. We find that a critical (minimum) value of $U_c = 1.1$ eV is required to produce the Mott insulating state. This critical value is significantly less than (therefore consistent with) values that have been suggested [8,18] as applicable to BNOO. This agreement reaffirms that Coulomb repulsion on top of strong SOC is an essential aspect of the mechanism underlying the insulating state. The compensation of the moments distinguishes between the various viewpoints, as we now describe.

The $|+1\uparrow\rangle$ state is pure-spin and pure-orbital moment, and within this state the z-component of the moment $\langle M_z\rangle = \langle +1\uparrow|(2S_z - \mathcal{L}_z)|+1\uparrow\rangle \equiv 0$ is compensated precisely by opposing spin and orbital contributions. This feature makes BNOO an unprecedented transition metal analog of the case of the Sm^{3+} d^5 ion [22] where $L = 2S$ and $M_z \sim 0$: the ion/cluster is magnetic ($J \neq 0$) but there is nearly vanishing total moment for a fixed direction of spin. The effect of mixing-in of other states by the kinetic hopping (quenching) is measured by the resulting exchange coupling $4\frac{t^2}{U} \sim 30$ meV ($t \approx 120$ meV, U=1.5-2 eV), i.e. it is small compared to other energies in the system. While the spin and orbital moments each depend fairly strongly on the value of U (table 1), the cancellation between the two remains near-complete. This cancellation is a nontrivial effect, since appreciable mixing-in of the $|0\downarrow\rangle$ state along (say) would degrade the spin moment without affecting the orbital moment.

Discussion. The small ordered moment was one of the principle questions about BNOO. From the point of view presented here, a small moment is *expected* and the question becomes rather: why is it as large as observed? Naively, this near-pure spin state is unexpected, given the strong SOC which is largely regarded as mixing (*not* separating out) spin and orbital moments, nevertheless it is an occurrence that has recently been anticipated. [23] At the level of description of the Hamiltonian eq. 3 in mean field approximation, we have a Curie-Weiss moment $\langle M^2\rangle^{1/2}$ = $\sqrt{7}\mu_B$ and an ordered FM moment of $\approx 0.04\mu_B$ (see table 4), which is only nonzero due to quenching. The
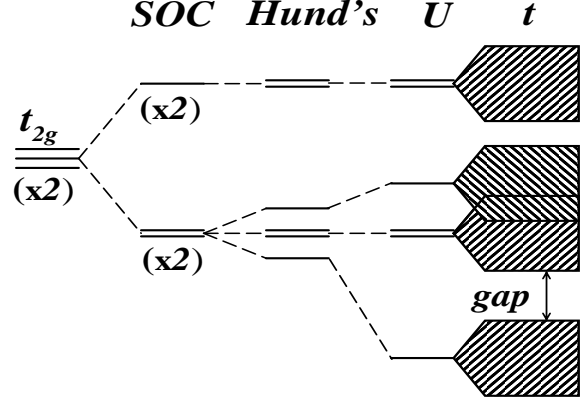
agreement with the observed values (near 0.7 and 0.2 μ_B, respectively) in absolute terms is not good, however one would expect a small ordered moment of 0.2 μ_B to be difficult to reproduce in a first principles manner. The degree of collinearity of $\vec{S}$ and $\vec{\mathcal{L}}$, which finally determines the moment, is sensitive to the environment. The magnitude of collinearity, $\| \vec{\mathcal{L}} \cdot \vec{S} \| / (\| S \| \| \mathcal{L} \|)$, is only 40% in the $J = \frac{3}{2}$ manifold anyway. Adding a crystalline anisotropy term $\gamma\mathcal{L}_z^2$ decreases it rapidly, by a further 35% for $\gamma = \xi$ and by 60% for $\gamma = 2\xi$ (this is orbital moment quenching). The quantum fluctuations are thus quite sensitive to the environment.

The matter of quantitative agreement of moments is actually a broader question: the related compound Ba_2CaOsO_6 (BCOO) with one more electron and S=1 and a cubic crystal structure is more conventional, yet it has a Curie-Weiss moment [24] of 1.61 μ_B that is also far below the spin-only value of 2.83 μ_B. The Re-based d^1 double perovskites Sr_2XReO_6, X = Mg and Ca, on the other hand, experience much smaller SOC and have moments equal to the spin only values and display structural distortions as the conventional picture would suggest. This distinction supports the involvement of strong spin-orbit coupling in both the small moment and the "restoration" of cubic symmetry in the heptavalent osmates BNOO and BLOO.

The magnetic ordering issue (BNOO is FM; isostructural and isovalent BLOO with almost identical volume is AFM) is a challenging and delicate question involving several complications. First, the *fcc* lattice itself can be considered one of the most frustrated. Frustration on the triangular lattice, with its edge-sharing triangles, is well known. Symmetric tetrahedra are frustrated, and the pyrochlore lattice of vertex-sharing tetrahedra is a well studied case of strong frustration. The *fcc* lattice can be pictured as one of space-filling, face-sharing tetrahedra.

Second, spin coupling between the OsO$_6$ clusters in BNOO proceeds through three distinct hopping processes $t_\sigma, t_\pi, t_\delta$ between anisotropic $\mathcal{D}_{xz} + i\mathcal{D}_{yz}$ cluster orbitals, and the behavior of the Curie-Weiss susceptibility reflects a net antiferromagnetic coupling. Such coupling is strongly frustrated on an fcc lattice, and the actual pattern of ordering can be a delicate problem. The difference between FM BNOO and AFM BLOO, based on some small detail, reflects the geometrical frustration and apparent competing couplings that must be expected in this structure. Note that the cousin S=$\frac{1}{2}$ compound Sr$_2$CaReO$_6$, even with the coherent structural distortion that relieves some of the frustration, has been shown to be a spin glass system. [26]

Thirdly, orbital ordering is also subject to frustration. [27] The surviving cubic structural symmetry of the Os d^1 ion is seems remarkable, but one must recognize that the "ferromagnetism" arising in a strongly coupled spin+orbital moment system lowers the electronic symmetry of the system. The question of whether this degree of freedom remains disordered (a combined 'spin-orbital liquid' within the FM phase), and thus serves to restore effective cubic symmetry, is a question that requires further study. In any case, frustration and large spin-orbital coupling are key issues in Ba$_2$NaOsO$_6$.

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